Activated carbon catalytic ozonation of oxamic and oxalic acids

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Abstract

The oxidation of hazardous organic compounds leads to the formation of several by-products, being oxalic acid and oxamic acid final oxidation products refractory to ozonation. The present work aimed to study the ozonation of those carboxylic acids in the presence of activated carbon at different solution pH. For comparative purposes, experiments of adsorption on activated carbon, ozonation, and ozonation in the presence of activated carbon were carried out. In order to clarify the reaction mechanism, some experiments were done in the presence of a radical scavenger. With the aim of evaluating the role of the activated carbon surface chemistry during the ozonation, two activated carbon samples were assessed. A significant synergistic effect between ozone and activated carbon was evidenced in the oxidation of oxalic acid. Oxamic acid was found to be refractory to oxidation at pH 7. On the other hand, at pH 3, the mineralization of oxamic acid was significantly enhanced by the presence of activated carbon. Generally, the presence of activated carbon during ozonation increased the rate of degradation of both carboxylic acids leading to mineralization. Best results were achieved with the most basic activated carbon. In both cases, the efficiency of activated carbon promoted ozonation decreases with the increase of solution pH.

1. Introduction

Ozonation processes have been widely and successfully used in the fields of water and wastewater treatments. More recently, the combination of ozone with homogeneous or heterogeneous catalysts in order to activate the decomposition of ozone or improve ozone reactions with several organic compounds has been investigated [1,2] and is still subject of intense research. Heterogeneous catalytic ozonation aims to enhance removal of more refractory compounds through the transformation of ozone into more reactive species and/or through adsorption and reaction of the pollutants on the surface of the catalyst. Although supported transition metals are trendy catalysts in ozonation processes, activated carbon (AC) itself has been found to be an attractive and promising alternative to the treatment of wastewaters containing dyes or other organic contaminants [3–9], including carboxylic acids [10,11].

Activated carbon is believed to promote the decomposition of aqueous ozone [12–16], leading to the formation of oxygenated active species that are responsible for enhancing the mineralization of organic compounds.

The ozonation of several hazardous organic compounds such as pesticides, dyes, aromatic hydrocarbons, etc., originates significant amounts of saturated organic compounds such as aldehydes, ketones and carboxylic acids. Due to the low reactive nature towards ozone, short chain carboxylic acids tend to accumulate in solution. Hence, single ozonation is not sufficient to achieve a high mineralization degree.

Oxalic acid has been identified as one of the most common final oxidation products from organic compounds degradation. The oxidation of organic compounds containing nitrogen functional groups can also result in the formation of oxamic acid [17,18] which is apparently more refractory to oxidation than oxalic acid. The low reaction rate constants reported in the literature for the ozonation of oxalic acid and their corresponding anions ($k < 0.04 \text{ M}^{-1} \text{ s}^{-1}$ at pH > 5 [19]) explain why such compounds always accumulate as final products when organic aqueous solutes are ozonized in water. The compounds of low reactivity towards ozone may be

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oxidized by secondary oxidants such as hydroxyl radicals produced during the decomposition of ozone in aqueous solution. In fact, oxalic acid reacts with $HO^\bullet$ radicals at a much higher rate ($k \approx 10^6$ M^{-1} s^{-1} [20]).

In a recent work (to be published) on the ozonation of some aromatic compounds promoted by activated carbon, oxalic acid was identified by us as one of the final oxidation products of benzenesulfonic and sulfanilic acids. In the latter case, also oxamic acid was detected. These compounds were responsible for great part of the final amount of total organic carbon (TOC) in solution. In this work, the activated carbon promoted ozonation of oxamic and oxalic acid was investigated. Although some data on the ozonation of oxalic acid in the presence of activated carbon has already been described in the literature [10], as far as we know, information on oxamic acid catalytic ozonation has not yet been presented. Our main goal was to study the catalytic ozonation of these two acids, in order to clarify the reaction mechanism and understand the influence of the activated carbon surface chemistry. As pH values influence not only ozone decomposition in aqueous solutions, but also surface properties of activated carbon and dissociation of organic molecules in water, two level of pH were studied.

2. Experimental

2.1. Materials

Oxalic acid (99%) and oxamic acid (96%) were obtained from Sigma–Aldrich. A commercial activated carbon, Norit GAC 1240 PLUS (sample AC_0), was submitted to an oxidation treatment in the liquid phase with HNO_3 6 M under boiling temperature during 3 h (sample $ACHNO_3$) [14]. The textural characterization of the materials was based on the N_2 adsorption isotherms determined at 77 K. The surface chemistry of the activated carbon samples was characterized by the determination of acidity and basicity, pH_{pzc}, and temperature-programmed desorption (TPD), as described elsewhere [21].

2.2. Kinetic experiments

The removal of oxalic and oxamic acids from aqueous solutions at different pH values was investigated in a slurry lab-scale reactor equipped with agitation and recirculation jacket. For comparative purposes, both adsorption on activated carbon and ozonation experiments in the absence of activated carbon were performed in the same system, under identical experimental conditions. Two activated carbons with different surface chemistries were assessed. The reactions were carried out at the natural pH of the acids solutions, which was approximately 3 in both cases, and at pH 7. In the latter case, a phosphate buffer solution (0.01 M) was used to maintain the solution pH. In each experiment the reactor was filled with 700 mL of acid solution 1 mM at the desired pH. In the adsorption and catalytic ozonation experiments, 350 mg of activated carbon (ground to a particle size of 100–300 μm) were introduced in the reactor. Ozone was produced from pure oxygen in a BMT 802X ozone generator. The experiments were performed at constant gas flow rate (150 cm^3 min^{-1}, measured at room T and P) and constant inlet ozone concentration (50 g Nm^{-3}). The concentration of ozone in the gaseous phase was monitored with a BMT 964 ozone analyzer. Ozone in the gas phase leaving the reactor was removed in a series of gas washing bottles filled with iodide potassium solution. The agitation was maintained constant at 300 rpm in order to keep the reactor content perfectly mixed and the temperature was set to 25 °C.

The concentration of both oxalic and oxamic acids was followed by HPLC using a Hitachi Elite Lachrom HPLC equipped with a diode array detector. The stationary phase was a YMC Hydrosphere C18 column (250 mm × 4.6 mm) working at room temperature, under isocratic elution with a mixture of water, acetonitrile and *o*-phosphoric acid at pH 2. The degree of mineralization was followed by TOC analysis in a Shimadzu TOC-5000A Analyzer.

3. Results and discussion

3.1. Characterization of activated carbons

The physical and surface chemical properties of the activated carbon samples used in this study are summarized in Table 1.

Liquid phase oxidations have been reported not to significantly change the textural properties of the activated carbon, when performed under controlled experimental conditions [22]. In fact, analysis of the characterization results obtained for samples AC_0 and $ACHNO_3$, shows that no major differences in the textural properties of these materials were observed. Oxidation of the activated carbon with HNO_3 leads to a substantial increase in volatiles content (results not shown). This is related to the amount of oxygen containing groups introduced on the activated carbon surface. As expected, the surface acidity increased for sample $ACHNO_3$ due to the introduction of several oxygen-containing functional groups, namely carboxylic acids, whereas the surface basicity decreased. Accordingly, this treatment yields samples with

Table 1
Characterization of activated carbon samples

Sample	S_{BET} (m² g⁻¹)	S_{meso} (m² g⁻¹)	V_{micro} (cm³ g⁻¹)	Acidity (μmol g⁻¹)	Basicity (μmol g⁻¹)	pH_{pzc}	CO[a] (μmol g⁻¹)	CO_2[a] (μmol g⁻¹)
AC_0	909	100	0.332	211	352	8.5	579	63
$ACHNO_3$	827	88	0.304	1003	77	3.0	2122	559

[a] Calculated by TPD spectra integration.

low pH_{pzc}. Comparatively, sample AC_0 has a moderate basic character and higher pH_{pzc}. According to the TPD results (Table 1), sample $ACHNO_3$ releases higher amounts of CO and CO_2 which indicates a greater content of surface oxygen-containing groups than sample AC_0.

It is known that both textural and surface chemical properties control the decomposition of ozone in water [14,16]. In this work, the behaviour of the two mentioned activated carbon samples, differing mainly in their chemical surface properties, is compared in the catalytic ozonation of two carboxylic acids (oxalic and oxamic acids) which are usual final oxidation by-products in the ozonation of organic pollutants.

3.2. Adsorption of oxalic and oxamic acids on activated carbon

It is understood that the surface chemistry of activated carbon plays a role in the decomposition of ozone in water into more reactive species [14,16]. Moreover, when working with organic compounds, it is expected that the adsorption capacity of the carbon samples towards these compounds also plays a key role during activated carbon promoted ozonation. On one hand, adsorption competes with the oxidation reaction to the removal of pollutants from the aqueous phase. On the other hand, the adsorption step may play a role in the mechanism of catalytic ozonation. For these reasons, adsorption studies of oxamic and oxalic acids were carried out separately on both activated carbon samples at different solution pH. The corresponding kinetic results are depicted in Figs. 1 and 2.

At the natural solution pH, which is around 3, approximately 19% of the oxamic acid is adsorbed on AC_0 after 120 min, while less than 5% is adsorbed on sample $ACHNO_3$. Fig. 1 also shows that at neutral pH, oxamic acid adsorption is negligible, especially on sample $ACHNO_3$.

Similarly to oxamic acid, oxalic acid uptakes are higher at pH 3 than at pH 7, regardless the nature of the activated carbon. As shown in Fig. 2, at pH 3 there is a huge difference in the behaviour of both activated carbon samples. After 120 min,
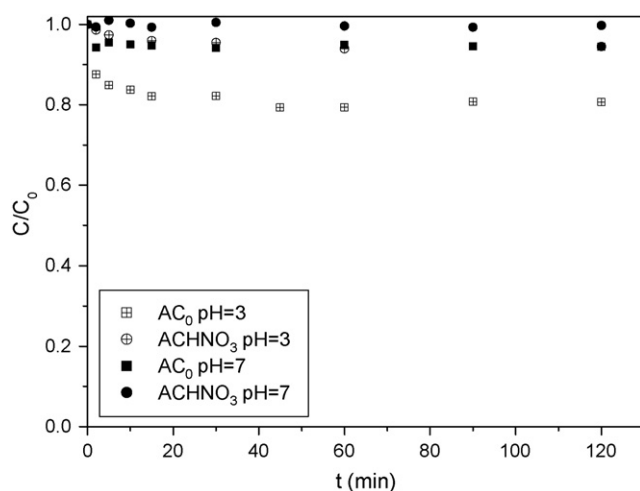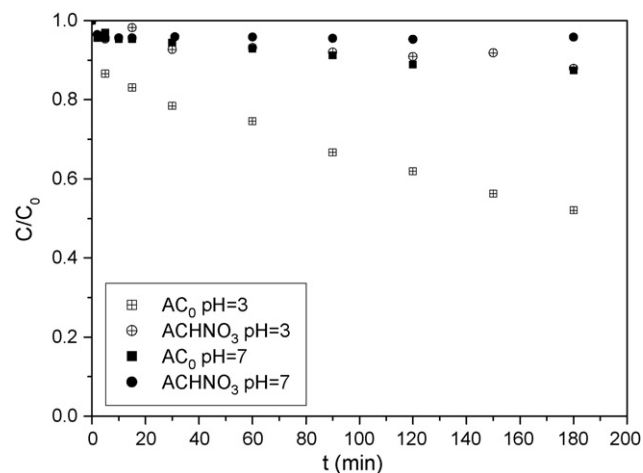

Fig. 2. Adsorption of oxalic acid on AC_0 and $ACHNO_3$ at different pH (C_0 = 1 mM; AC = 0.5 g/L).

sample AC_0 adsorbs 38% of oxalic acid from solution, while, in the same conditions, sample $ACHNO_3$ removes only 9% of it.

The fact that both acids are better adsorbed at acidic pH than at neutral pH might be due, to a great extent, to the different species present in water, which have different hydrophilicity. Significant changes in solubility are observed with pH variation for organic acids and bases. Depending on the solution pH, those might be in the molecular or ionic form. Since charged solutes are able to strongly interact with water, the charged form of an acid or base can be much more hydrophilic, thus being less prone to be adsorbed on activated carbon. For oxalic acid (pKa_1 = 1.23; pKa_2 = 4.19), increasing pH results in an increase in the fraction of ionic species, as the acid deprotonates to form the conjugated base. The increase in the pH leads to an increase in the hydrophilicity of the dissolved species (the common logarithm of the distribution coefficient K_{ow} decreases from -1.92 to -8.73 when pH increases from 3 to 7). As a consequence, the dissolved species may have a much lower affinity towards activated carbon surface at pH 7.

Oxamic acid molecule has a basic and an acid functional group (pKa_1 = 2.5 for the carboxylic group and pKa_2 = 11.8 for NH_3^+) [17]. According to this, at pH 3 dissolved oxamic acid is approximately equally distributed in the following species: $HOOC–CONH_3^+$ and $^-OOC–CONH_3^+$, while at pH 7 the latter species predominates in solution. The presence of both charged groups highly increase the hydrophilicity of the oxamic acid, which may explain the lower adsorption on activated carbon at pH 7.

Another possible explanation for the decrease in both acid uptakes when pH increases is the presence of phosphate ions in solution, necessary to buffering, which may compete with both oxalic and oxamic acid for adsorption on the activated carbon surface. Actually, it was observed that at pH 3 the adsorption of oxamic acid on sample AC_0 slightly decreased when it was carried out in the presence of a phosphate solution, confirming the interference of the phosphate buffer solution during adsorption.

It was also observed that, regardless of the pH, sample AC_0 always presented higher adsorption capacity than sample

Fig. 1. Adsorption of oxamic acid on AC_0 and $ACHNO_3$ at different pH (C_0 = 1 mM; AC = 0.5 g/L).

ACHNO$_3$. At pH 3, the surface of sample AC$_0$ is positively charged (pH$_{pzc}$ > pH) while sample ACHNO$_3$ has a neutral net charge surface. Thus, anionic species in solution have higher affinity to activated carbon AC$_0$ due to electrostatic interactions. At pH 7, ACHNO$_3$ surface becomes negatively charged (pH$_{pzc}$ < pH) increasing electrostatic repulsive interactions between the carbon surface and anionic species in solution. This is valid especially for oxalic acid that at pH 7 is totally deprotonated. The results obtained are consistent with what has been stated for the adsorption of organic compounds [23]. In general, basic carbons such as sample AC$_0$ present better adsorption capacities than more acidic ones when solutes are present either in their molecular or anionic form.

3.3. Ozonation of the selected carboxylic acids

The removal of dissolved oxamic and oxalic acids by ozonation in the presence or absence of activated carbon was studied separately at pH 3 (natural pH of the solutions) and pH 7 (buffered solutions).

3.3.1. Oxamic acid

Oxamic acid was shown to be highly refractory towards ozonation at pH 3. According to Fig. 3, the addition of a small amount of activated carbon resulted in a major increase in the removal of oxamic acid from solution.

The degree of mineralization is also an important parameter to monitor in this type of oxidation processes, as it represents a measure of the removal of organic matter from water. In this work, the mineralization was checked by measuring the total organic carbon (TOC) of the solution along time (not shown). The TOC concentration determined experimentally was in good agreement, within the experimental error, with that calculated from the residual oxamic acid concentration during ozonation, and was consistent with the absence of organic intermediates in the chromatograms. During activated carbon promoted ozonation, oxamic acid is mutually adsorbed and mineralized. According to the literature, the ozonation of –NH$_2$ containing compounds might lead to the formation of NO$_3^-$ or/and NH$_4^+$. In the experimental conditions used in this work, NH$_4^+$ was detected in solution but no measurable NO$_3^-$ concentrations were detected during the oxidation of oxamic acid.

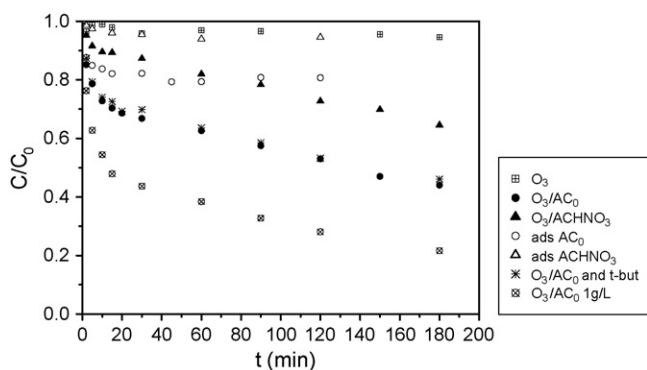Fig. 3. Evolution of the dimensionless concentration of oxamic acid at pH 3 (C$_0$ = 1 mM, AC = 0.5 g/L or 1 g/L, C$_{tert}$-butanol = 10 mM).

Adsorption results, previously discussed, showed that removal of oxamic acid by adsorption on sample ACHNO$_3$ was quite low. Nonetheless, the combination of O$_3$ and ACHNO$_3$ resulted in a significant increase in the removal of oxamic acid. These observations are important to reinforce the existence of a significant synergistic effect between ozone and activated carbon. In this case the result obtained is more than just a sum of the two contributions (ozonation and adsorption); thus, the oxidation of oxamic acid can be attributed to a catalytic effect. The difference observed between the results obtained with samples AC$_0$ and ACHNO$_3$ could be correlated to the role of the surface chemistry of the activated carbon on the ozone decomposition [14] and/or to the higher adsorption capacity of sample AC$_0$ in opposition to ACHNO$_3$.

As far as activated carbon catalytic ozonation is concerned, Jans and Hoigné [15] reported that the decomposition of ozone in water in the presence of an activated carbon or a carbon black, yields hydroxyl radicals in the aqueous phase. In order to look ahead relatively to the mechanism of oxamic acid catalytic ozonation, an experiment was carried out in the presence *tert*-butanol (C = 10 mM), a well known hydroxyl radical scavenger, which has been reported not to significantly adsorb on activated carbon [10]. *tert*-Butanol reacts very rapidly with hydroxyl radicals ($k = 5 \times 10^8$ M^{-1} s^{-1}) [24] and very slowly with ozone ($k = 0.03$ M^{-1} s^{-1}) [25]. As shown in Fig. 3, the ozonation of oxamic acid catalyzed by AC$_0$ was not influenced by the presence of *tert*-butanol. Assuming that this alcohol is an effective HO$^\bullet$ radical scavenger, and knowing that oxamic acid is not oxidized by direct ozonation, it can be concluded that, under these conditions, the oxidation of oxamic acid occurs mainly trough reactions on the surface of the activated carbon. This fact would also explain why sample ACHNO$_3$ has a smaller activity in this reaction. Due the high amount of oxygenated surface groups, which have an electron withdrawing effect, sample ACHNO$_3$ has a lower electron density when compared to sample AC$_0$. As a result, both oxamic acid and ozone molecules have less affinity towards sample ACHNO$_3$. As shown in Fig. 3, the increase in activated carbon amount from 0.5 g/L to 1 g/L had a positive effect in the oxidation of oxamic acid, thus reinforcing the importance of the available surface area in the reaction mechanism.

The influence of the presence of a phosphate buffer solution, used in the experiments at pH 7, was tested in the ozonation of oxamic acid in the presence of AC$_0$ at pH 3. As can be observed in Fig. 4, the presence of the mentioned phosphate solution not only decreased adsorption (as previously reported) but had also a significant effect on the catalytic ozonation of oxamic acid. According to the previous reasoning, it is probable that the decrease in the oxidation rate of oxamic acid is mainly due to the fact that phosphate ions compete with oxamic acid and ozone towards adsorption on activated carbon surface, weakening its catalytic effect.

Oxamic acid was found to be refractory to single ozonation at pH 7 (Fig. 5). This observation was not predictable since ozone self-decomposition into oxygen radical species is initiated by the presence of HO$^-$ ions [26]. As discussed before, this effect is believed to be enhanced in the presence of
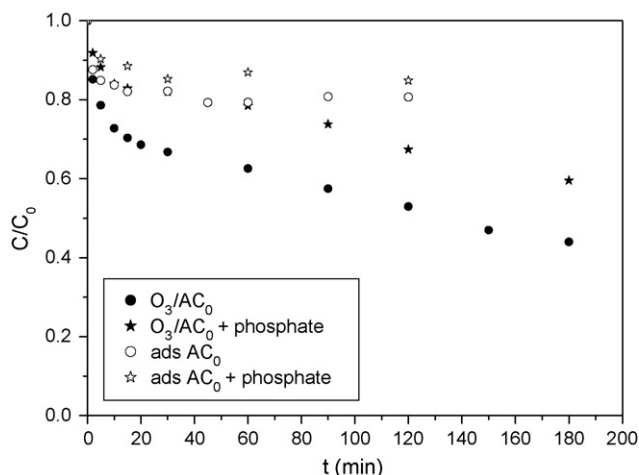
Fig. 4. Influence of the phosphate solution on the evolution of the dimensionless concentration of oxamic acid at pH 3 ($C_0 = 1$ mM, AC = 0.5 g/L).
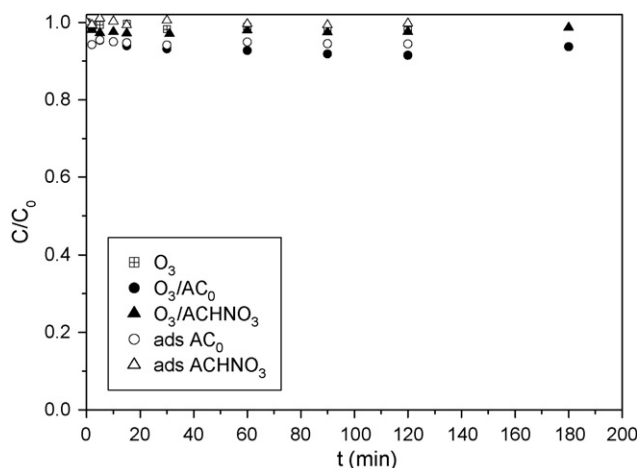

Fig. 5. Evolution of the dimensionless concentration of oxamic acid at pH 7 ($C_0 = 1$ mM, AC = 0.5 g/L).

activated carbon. Nevertheless, at this pH, single ozonation of oxamic acid resulted in a removal of only 2% after 120 min of reaction. In addition, the adsorption of this acid on samples AC_0 and, particularly, $ACHNO_3$ was negligible, as discussed in the previous section.

In this case, the addition of activated carbon to the process was not effective and the increase observed in the removal of oxamic acid was mainly due to the contribution of adsorption. Similar results were obtained during the ozonation in the presence of AC_0 at higher pH. Apparently, at neutral and basic pH, oxamic acid is highly resistant both to molecular ozone and hydroxyl radicals attack and is not significantly oxidized. At this range of pH, oxamic acid is mainly present as a zwitterion ($^-OOC–CONH_3^+$), which is highly hydrophilic and stable in water. According to Leitner et al. [17], who studied the removal of oxamic acid with γ-irradiation, this fact and the absence of C–H bonds explains its small reactivity towards $HO^\bullet$ radicals. Even though oxamic acid can be mineralized by $HO^\bullet$ radicals, at neutral pH, its oxidation requires a 100 times higher $HO^\bullet$ dosage than most of the organic compounds [17].
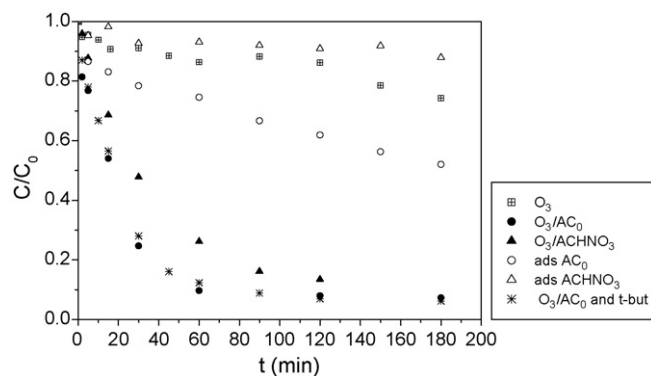

Fig. 6. Evolution of the dimensionless concentration of oxalic acid at pH 3 ($C_0 = 1$ mM, AC = 0.5 g/L, $C_{tert\text{-butanol}} = 10$ mM).

3.3.2. Oxalic acid

The ozonation of oxalic acid ($C_0 = 1$ mM) was carried out at pH 3 in the first place. The results obtained are depicted in Fig. 6.

It was observed that the mineralization of oxalic acid was significantly enhanced by the addition of activated carbon. The simultaneous use of ozone and activated carbon resulted in the removal of 92 and 86% of dissolved oxalic acid, after 120 min, for samples AC_0 and $ACHNO_3$, respectively. Thus, a significant synergistic effect between ozone and activated carbon is evidenced in the oxidation of oxalic acid. As expected, samples AC_0 and $ACHNO_3$ originated different results, which could be explained by a sum of two effects: AC_0 has a higher adsorption capacity towards oxalic acid than sample $ACHNO_3$ and a superior capability to enhance the catalytic decomposition of ozone into surface radical species and/or oxygen containing radicals, such as $HO^\bullet$, in solution. The ozonation of oxalic acid in the presence of AC_0 at pH 3 was not affected by the presence of the radical scavenger *tert*-butanol (Fig. 6). This leads to the conclusion that, at these conditions, the catalytic ozonation of oxalic acid occurs mainly on the surface of the activated carbon and is not a direct result of a higher concentration of radical species in solution. These results are not in agreement with those reported by Beltrán et al. during the activated carbon promoted ozonation of oxalic acid at pH 2.5 [10], where the presence of *tert*-butanol significantly inhibited the oxidation rate of oxalic acid compared to the activated carbon catalytic ozonation without the radical scavenger.

According to the literature and to our own results, the oxidation of oxalic acid leads to complete mineralization, i.e., there is no formation of organic intermediates. Therefore, total organic carbon concentration determined experimentally ought to be in agreement with that calculated from residual concentration of the oxalic acid. This was consistent with the results obtained in this investigation.

Similarly to what happened at pH 3, the simultaneous use of ozone and activated carbon at pH 7 is definitely advantageous for the oxidation of oxalic acid. According to the results depicted in Fig. 7, oxalic acid elimination increased up to 69 or 90%, after 120 min of reaction, when respectively samples $ACHNO_3$ or AC_0 were used during ozonation reactions.

In conformity with the mechanism for ozone decomposition in water, the increase in pH leads to a faster decomposition of
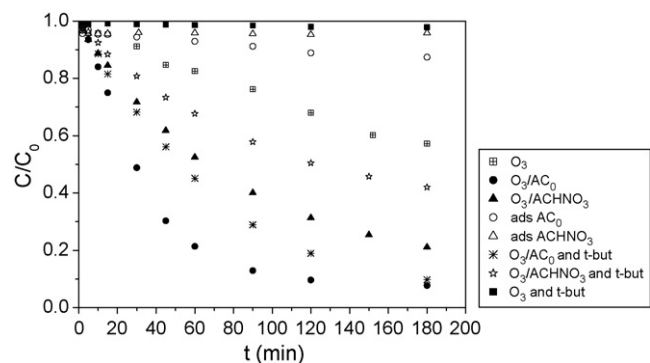
Fig. 7. Evolution of the dimensionless concentration of oxalic acid at pH 7 ($C_i = 1$ mM, AC = 0.5 g/L, $C_{tert\text{-butanol}} = 10$ mM).

ozone into oxygen radical species leading to the formation of HO$^\bullet$ radicals. Actually, when comparing experimental data on oxalic acid single ozonation, at the two pH values studied, a higher removal rate was observed at pH 7. When single ozonation was carried out in the presence of *tert*-butanol, almost no oxalic acid mineralization was observed, which confirms that the homogeneous oxidation of oxalic acid practically only occurs via HO$^\bullet$ radicals.

Contrary to what happened at pH 3, it was observed that the presence of *tert*-butanol inhibits the catalytic ozonation of oxalic acid comparatively to the same reaction without *tert*-butanol (Fig. 7). This effect was observed for AC$_0$ and ACHNO$_3$. This suggests that the reaction mechanism involves the formation of hydroxyl radicals that are scavenged in the presence of *tert*-butanol, resulting in a decrease of the ozonation rate of oxalic acid. Simultaneously, surface reactions are assumed to occur as well. In conclusion, the experimental results suggest two different pathways in the catalytic ozonation of oxalic acid in the presence of activated carbon: one occurs on the surface of the activated carbon, involving adsorption, surface reaction and desorption steps; the other occurs in the bulk liquid, involving reactions between highly oxidant species, resulting from ozone decomposition, and dissolved oxalic acid.

When comparing the results from ozonation in the presence of AC obtained at both pH 3 and 7, it is clear that better results are achieved at acidic pH. It is known that the pH not only influences ozone decomposition in aqueous solutions, but also controls the surface properties of activated carbon and the dissociation of organic molecules in water. As said before, a higher pH accelerates the decomposition of ozone into more reactive species that are likely to participate in the mechanism of oxalic acid oxidation. However, at acidic conditions oxalic acid has a higher affinity towards activated carbon than at higher pHs, as previously explained. Therefore, adsorption seems to represent an important path in the activated carbon catalytic ozonation of carboxylic acids.

3.4. Reaction mechanism

According to the experimental results obtained in this work there is strong evidence that the ozonation of both carboxylic acids occurs through a catalytic mechanism involving surface

and bulk reactions. It is visible that at pH 7 hydroxyl radicals are partially responsible for the mineralization of oxalic acid in solution. Due to this evidence and to the high instability of ozone in water, which decomposes through a radical chain mechanism, homogeneous oxidation reactions have to be considered.

Regarding the decomposition of ozone in aqueous solution, it is established that it is initiated by the presence of HO$^-$ ions; so pH plays a major role in this process:

$$O_3 \xrightarrow{HO^-} HO^\bullet \qquad (1)$$

As said before, several authors have reported that activated carbon accelerates the decomposition of ozone [12–16]. It is consensual that both textural and surface chemical properties influence that decomposition, but doubts on the mechanism still remains. According to the literature, two possible pathways can explain the decomposition of O$_3$ in the presence of activated carbon. The first one assumes that activated carbon acts as an initiator of the decomposition of ozone yielding free radical species, such as HO$^\bullet$ in solution [15]:

$$O_3 \xrightarrow{AC} HO^\bullet \qquad (2)$$

Another possibility is the adsorption and reaction of ozone molecules on the surface of the activated carbon, yielding surface free radicals [12]:

$$O_3 + AC \rightarrow AC - O \qquad (3)$$

where AC $-$ O stands for any oxygen-containing active species on the surface of the activated carbon, including HO$^\bullet$ radicals. The oxidation of carboxylic acids is thus possible to occur on the surface of the activated carbon, between the adsorbed reagent (R) and surface radical species, according to the following steps:

$$R + AC \rightarrow AC - R \qquad (4)$$

$$AC - R + AC - O \rightarrow P \qquad (5)$$

As this mechanism has no experimental evidence, it is necessary to consider that adsorbed species might also react with dissolved ozone, reaction (6), or hydroxyl radicals from the aqueous phase, reaction (7). Similar assumptions have been presented by Beltrán et al. [27], concerning the ozonation of pyruvic acid catalyzed by activated carbon.

$$AC - R + O_3 \rightarrow P \qquad (6)$$

$$AC - R + HO^\bullet \rightarrow P \qquad (7)$$

As already mentioned, the rate constant of the reaction between carboxylic acids and molecular ozone is quite low. The oxidation of these species in aqueous solution occurs via a radical chain mechanism where HO$^\bullet$ radicals are the main intervenient. Therefore, a homogeneous reaction mechanism must be considered too:

$$R + HO^\bullet \rightarrow P \qquad (8)$$

As shown in Figs. 3 and 6 the presence of the radical scavenger (*tert*-butanol) did not inhibit the oxidation of oxamic

and oxalic acids at pH 3. Therefore, at those conditions, both reactions (7) and (8) are not likely to occur. At pH 7 the existence of a reaction path involving HO$^{\bullet}$ radicals was experimentally evidenced in oxalic acid catalytic ozonation. Even so, this mechanism does not explain the results obtained for oxamic acid at pH 7, which are probably related to the chemical nature of this compound.

Steps (2), (3) and (4) entail the dependence of the proposed mechanism on the surface properties of the activated carbon, as it influences both adsorption of reactants and interaction with ozone molecules, as previously explained.

4. Conclusions

The simultaneous use of ozone and activated carbon yields significant increases of oxalic and oxamic acid removal from water when compared to single ozonation and single adsorption, proving the existence of a catalytic reaction mechanism. Exception was observed for oxamic acid, as it was found to be resistant to oxidation at neutral and basic pH. Generally, the presence of activated carbon during ozonation increases the rate of degradation of both carboxylic acids leading to mineralization. A higher basicity of the activated carbon enhances the efficiency of this treatment process.

The low reactivity of these compounds towards direct ozonation and the non-existent influence of the radical scavenger at pH 3 suggest that the oxidation occurs mainly through reactions on the surface of the activated carbon. In the case of oxalic acid at pH 7, the results can be explained from a mechanism involving both surface reactions and bulk reactions between the organic solute and hydroxyl radicals.

For both carboxylic acids, the efficiency of activated carbon promoted ozonation decreases with the increase of solution pH. At least in part, this might be related to a higher solubility of solutes at neutral and basic conditions, and to a consequent lower affinity towards activated carbon surface.

Acknowledgments

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